

V667.15 ~~NOV 11 1977~~

N17631 #3  
Sep

Recherche

No. 766,196



ISSUED Aug. 29, 1967  
CLASS 117-126

# CANADIAN PATENT

LAMP COATING

Russell M. Luck, Monroeville, Pennsylvania, U.S.A., and  
Gordon C. Gainer, Pittsburgh, Pennsylvania, U.S.A.

Granted to Westinghouse Electric Corporation, Pittsburgh,  
Pennsylvania, U.S.A.

IDS #4

APPLICATION No. 952,586  
FILED Feb. 18, 1966  
PRIORITY DATE Mar. 3, 1965 (436,799) U.S.A.  
No. OF CLAIMS 10

H 877

766196

This invention relates to lamp coatings and, more particularly, to coatings which are adapted to be applied to the exterior surface of a lamp envelope for either indoor or outdoor use.

In the practices of the prior art, colored incandescent lamps have been manufactured by the many millions, modifying the color-imparting coating in accordance with the coating appearance desired and the type of use intended for the lamp. In one type of Christmas lamp intended  
10 for indoor use only, a colored or pigmented cellulose acetate lacquer has been applied to the outside of the finished clear lamp by a dip coating procedure. If such a coating is subjected to the temperature and humidity extremes of outdoor use, however, the coating loosens and peels because of moisture effects and temperature extremes

For Christmas lamps intended for outdoor use, the color coating has been applied as an alcoholic suspension of a pigment in an inorganic binder sprayed onto the inside surface of the lamp envelope. Such a coating  
20 is well suited for outdoor use since being on the inside of the lamp envelope, it is never directly exposed to moisture and weather effects. However, the coating is quite expensive since a lengthy conditioning or baking period is required in the manufacturing process, in order to remove gaseous impurities and moisture from the internally applied coating, thereby making the lamp relatively expensive.

In a third type of colored incandescent lamp, a ceramic coating (colored glass frit) has been applied to  
30 the outside surface of the lamp. Such coatings are quite

766196

satisfactory from the standpoint to weatherability, but are quite expensive to apply and a relatively large number of rejects are produced due to imperfect coatings.

Since the foregoing different types of coatings all have to be applied by different processes, these unduly complicate the manufacturing techniques and, in addition, require an excessive amount of costly equipment and floor space. From the standpoint of cost of application, the lowest cost coating is a lacquer coating which is applied on the outside of the finished lamp by means of a dip-coating process. It would thus be desirable from the standpoint of cost and performance to have a universal indoor-outdoor coating which could be applied to the exterior surface of an incandescent lamp by a simple dip process.

It is the general object of the present invention to provide an inexpensive external coating for an incandescent lamp envelope which is resistant to sunlight and atmospheric moisture and humidity.

It is a further object to provide an inexpensive exterior incandescent lamp coating which is thermally stable and resistant to appreciable degradation through oxidation, even when exposed to high temperatures for prolonged periods of time.

It is another object to provide an inexpensive exterior incandescent lamp coating which is resistant to thermal cycling due to rapid changes in temperature such as are encountered when the ambient temperatures are quite low and the lamp is energized.

It is an additional object to provide a plastic exterior lamp coating which possesses good adhesion to the

766196

glass envelope even in the presence of moisture, ice, or high humidity.

It is yet another object to provide an exterior lamp coating which essentially comprises organic material which will not exhibit any tackiness on the surface at the lamp envelope operating temperature.

It is still another object to provide an exterior lamp coating which is particularly adapted to be applied by a high speed dipping procedure and will not  
10 abrade under the conditions of operation to which the lamp is subjected.

It is a further object to provide an exterior lamp coating which displays a good surface gloss and flows out when applied so that its appearance will be commercially acceptable.

The foregoing objects of the invention, and other objects which will become apparent as the description proceeds, are achieved by providing a hollow, light-transmitting glass member, such as an incandescent lamp  
20 envelope, which is adapted to surround a source of radiations such as an incandescent filament. A coating is carried on the external surface of the glass member and comprises (a) a polymer consisting essentially of polymethylmethacrylate which has a tack point temperature of at least 170°C; (b) from 0.1% to 10% by weight of the polymethylmethacrylate resin of an organofunctional silane which behaves as a coupling agent wherein the organic functional groups of the silane are reacted with the polymeric matrix of the coating, and silicon functional groups of  
30 which are reacted with the surface portion of the glass member; and (c) from 2% to 20% by weight of ther-

766196

polymethylmethacrylate resin of an additive organic substance which is at least substantially transparent, has a boiling temperature at atmospheric pressure of at least 250°C, and is completely soluble in the polymethylmethacrylate within the temperature range of from -40°C to 170°C. The additive organic substance is introduced to prevent crystallization of the polymethylmethacrylate polymer in the coating, which, when it occurs, is ruinous in a lamp coating.

10 For a better understanding of the invention, reference should be made to the accompanying drawing wherein the sole figure illustrates an elevational view of a Christmas tree lamp, with a portion of the lamp envelope shown in section to illustrate the coating of the present invention.

20 With specific reference to the form of the invention illustrated in the drawing, the lamp 10 comprises a sealed glass envelope 12 which encloses either a vacuum or an inert gas. A conventional stem 14 terminates in a press portion 16 through which lead-in conductors 18 are sealed, and an incandescent filament 20 is supported between the inwardly extending extremities of the lead-in conductors 18. The lead-in conductors electrically connect to a conventional screw-type base 22 which is affixed to the neck portion of the envelope 12. The stem seal can be replaced by a conventional butt seal if desired.

30 The lamp coating 24 is modified polymethylmethacrylate and is applied as a generally uniform layer to the exterior surface of the envelope 12. The lamp coating 24 consists essentially of selected

766196

polymethylmethacrylate which has a tack point temperature of at least 170°C, and an inherent viscosity of 0.44 or greater, with an addition of a small amount of an organofunctional silane and an additive organic substance having particular characteristics, as will be specified hereinafter.

With respect to the minimum tack point temperature of the polymethylmethacrylate, this is required to be at least 170°C that in order that dust or lint or similar substance will not adhere to the exterior coating, when the lamp is operated. This tack point temperature is readily determined by coating a slide or similar glass member or a given style of lamp with the polymethylmethacrylate and exposing it to the specified temperature of 170°C, for a period of 15 minutes, usually by energizing the coated lamp. A small piece of tissue paper is lightly pressed onto the heated coating and then pulled away. The paper should be readily removable from the coating without any evidence of sticking or deposition of lint or fibre. It was found that this minimum specified tack point temperature is closely related to the molecular weight (and thus to the inherent viscosity) of the polymethylmethacrylate, with the higher the molecular weight of this material, the higher the tack point temperature. As an example of evidence of the proper molecular weight of a suitable polymer, a polymethylmethacrylate having an inherent viscosity of at least 0.44 was found to be acceptable. Inherent viscosity as defined herein is the viscosity of a solution containing 0.25g. of polymer in 50 ml. of chloroform, measured at 25°C., using a #50 Cannon Fenske Viscometer. Also see pages 80-81 of Billmeyer, "Textbook of Polymer Science", Interscience Publishers, New York, (1962). The logarithm of inherent

66196

viscosity is directly proportional to the logarithm of weight average molecular weight. Thus, inherent viscosity is a convenient basis for comparing molecular weights.

While such a methylmethacrylate polymer will be quite stable under the temperature and weather extremes to which it is exposed, if coated alone onto the glass bulb its adhesion to the glass will be relatively poor. In order to improve the adhesion of the polymer to the glass bulb, there is included therewith from 0.1% to 10% by weight of the polymethylmethacrylate of an organofunctional silane, wherein organic functional groups of the silane are reacted with the polymethylmethacrylate and silicon functional groups are reacted with the surface portions of the glass member. A very satisfactory organofunctional silane is N- $\beta$ -aminoethyl- $\gamma$ -aminopropyltrimethoxysilane. Other organofunctional silanes which are also quite satisfactory are  $\gamma$ -methacryloxypropyltrimethoxysilane,  $\gamma$ -glycidoxypropyltrimethoxysilane or vinyltriethoxysilane. These silanes can be used alone or in combination. The characteristics of these organofunctional silanes are such that the ambifunctional groups thereof will react with both the surface of the glass and the polymethylmethacrylate in order to act as an adhesion promoter or coupling agent between the surfaces of its glass and the polymer. A discussion of such coupling of agents is found in "Handbook of Adhesives" published by Reinhold, New York, 1962, Chapter 33 by W. J. Eakins.

The high molecular weight polymethylmethacrylate as modified by the foregoing silane adhesion promoters is quite suitable in performance for short periods of operation. In prolonged testing under the temperature

766196

extremes and temperature gradients to which the lamp coatings are subjected, however, the polymethylmethacrylates display a tendency toward growth of crystals within the coating film due to polymer crystallization. In order to prevent this crystal growth, there is added to the polymethylmethacrylate and the mixed adhesion-promoting silane from 2% to 20% by weight of the polymer of an additive organic substance which is at least substantially transparent, has a boiling temperature at atmospheric pressure of at least 250°C, and is completely soluble in the polymethylmethacrylate within the temperature range of about -40°C to 170°C, which temperature range represents the temperature extremes to which the coating can be subjected. The exact functioning of the additive "crystal preventing" substance is not clear, but every substance falling within the foregoing general categorization is operative. As an example, the following additives can be used and are preferred:

butyl benzyl phthalate; chlorinated biphenyl; butyl phthalyl butyl glycolate; N-ethyl toluene sulfonamide; tricresyl phosphate; or polyisobutylmethacrylate. Many materials may be used as additives in order to prevent crystal growth in the coatings and examples are as follows: methyl abietate; dibutoxyethylphthalate; dibutyl sebacate, dibutyl tartrate; di-(2-ethylhexyl) azelate; di-(2-ethylhexyl) phthalate; pentaerythritol esters; isooctylbenzyl phthalate; isodecyl benzyl phthalate; castor oil; dioctyl phthalate, dibutyl phthalate; or chlorinated biphenyls. This listing of possible additives is by no means inclusive, of course, but represents the range of additive materials which will function as crystal inhibitors.

Summarizing the composition of the basic coating,



766196

it essentially comprises a three component system, namely, a selected polymethylmethacrylate polymer having an inherent viscosity of 0.44 or greater, the organofunctional silane, and the additive substance. While the organofunctional silane can be used in amounts of from 0.1% to 10% by weight of the polymethylmethacrylate vehicle, it preferably is used in amounts of from 0.3% to 3% by weight of the polymer with a preferred example being about 0.5% by weight of the polymethylmethacrylate. While the additive  
10 organic substance can be used, in amounts of from 2% to 20% by weight of the polymethylmethacrylate, it preferably is used in amounts of from 5% to 15% by weight of the polymer. A preferred example for the additive substance is about 10% by weight of the polymethylmethacrylate.

While the main constituent of the present lamp coating is essentially polymethylmethacrylate, other slightly modified polymethylmethacrylate polymers can be utilized in a coating. An example of such a type is a polymethylmethacrylate containing, for example, 5% by  
20 weight of acrylamide as a comonomer. Other comonomers can also be used. The foregoing coating is substantially transparent. A specific example for preparing such a transparent coating follows: 2,375 grams of a solution of polymethylmethacrylate (having an inherent viscosity of 0.442) is dissolved in solvent consisting of a mixture of toluol, methylethyl ketone and butanol in the volume ratio of 50/40/10. The solution exhibits a viscosity of about 240 cps at 25°C. and is 30% solids, by weight. To this solution is added 137.5 grams of powdered poly-  
30 methylmethacrylate having an inherent viscosity of about 1.20. There is then added 425 grams of acetone, 15 grams of

766196

$\gamma$ -glycidoxypropyltrimethoxysilane and 10% by weight of the total polymer of butyl benzyl phthalate. The resulting lacquer is milled to a uniform consistency. The lamps are dip coated with the lacquer and thereafter baked at a temperature of 80°C for 45 minutes. The resulting coating is clear and lamps coated therewith can be used either for outdoor or indoor application with no deleterious effects.

The usual lamp coating is translucent, or colored, or both. A colored coating is readily achieved by adding  
10 a coloring substance in the form of a dye, or a pigment, or a mixture of a dye and a pigment to the lacquer. The coloring substance, by the preferred procedure, is evenly dispersed throughout the lacquer or dissolved in the lacquer by ball milling for a period of about 15 hours. There may also be added to the lacquer a predetermined amount of finely divided, light-scattering substance, in order to provide the coating with a desired degree of translucency.

As a specific example, benzidine yellow in the amount of 28 grams and phthalocyanine green in the amount  
20 of 70 grams when added to the foregoing example will provide a green pigmented lacquer. The lacquer can be made more translucent by adding thereto 48 grams of finely divided titanium dioxide, which serves a light-scattering function. A blue pigmented lacquer can be made by adding to the foregoing example of the clear lacquer 45 grams of phthalocyanine blue. This lacquer can be made more translucent by the addition of 70 grams of titanium dioxide. A pink lacquer can be formulated by adding 1.4 grams of  
30 diazo red to the foregoing clear lacquer example and this lacquer can be rendered translucent by adding 69 grams of finely divided titanium dioxide. An orange lacquer can

766196

be fabricated by adding 2 grams of the diazo red and 63 grams of "Cromophtal Gold" or chrome yellow thereto. The lacquer can be rendered more translucent by adding 63 grams of titanium dioxide. A red lacquer can be compounded by adding 91 grams diazo red to the clear lacquer together with 18.0 grams of titanium dioxide pigment and a blue lacquer can be fabricated by adding 44 grams phthalocyanine blue thereto, in conjunction with 70.0 grams of white titanium dioxide pigment.

- 10           In order to form transparent colored coatings, a dye soluble in the polymer is preferably used in place of a pigment. As an example, to form a blue transparent lacquer coating composition, 5.5 grams of blue azo type dye are added to the above described clear lacquer.

As a second example of transparent colored coatings, 600 grams of the foregoing polymethylmethacrylate solution using the 50/40/10 toluol/methyl ethyl ketone/butanol solvent has dissolved therein 35 grams of solid polymethylmethacrylate having an inherent viscosity of 1.20.

- 20   A similar solution can be obtained by mixing 600 grams of Rohm and Haas "Acryloid" A-2LLV and 35 grams of DuPont "Lucite" #2041. To this clear lacquer solution is added 87 grams of acetone, 3.8 grams of the indicated  $\gamma$ -glycidioxypropyltrimethoxysilane and 18.9 grams of butyl benzyl phthalate. A red transparent lacquer can be prepared by milling an azo type scarlet dye into the resulting lacquer and fuchsia, amber or green transparent lacquers can be readily fabricated by milling appropriate azo dyes into these lacquers.

- 30           All of the foregoing examples can be readily applied to the exterior surface of the finished incandescent

766196

lamps by a dip coating process and the resulting coatings will have a substantially uniform thickness of from 1 to 2.5 mils. The thickness of the coating will depend upon minor variations in viscosity in the coating lacquer and the manner of evaporating solvents. This indicated thickness is not intended to be limiting, however, and may be varied considerably. The resulting coated lamps all have a tack temperature of more than the indicated 170°C. Resistance of the coatings to thermal shock is excellent and they will withstand repetitive cycles from 150°C to a plunge in ice water. The long-time moisture resistance, hydrolytic stability and adhesion to glass of the coatings is excellent and they will withstand immersion in boiling water for long periods of time with no ill effects. The coatings can also be aged at relatively high temperatures without displaying any degradation either in color or physical characteristics throughout the life expectancy of the longest life lamp types. Satisfactory color retention and freedom from discoloration has been obtained in which pigmented coatings, after, for example, 3000 hours of energized operation on 10 watt night lights. The coatings are sufficiently hard to resist any tendency to abrade and they display a high gloss.

It will be recognized that the objects of the invention have been achieved by providing a lamp coating which can be applied to the exterior surface of all types of lamps and which coating has excellent resistance to sunlight and atmospheric moisture and humidity, is thermally stable when subjected to relatively high temperatures for prolonged periods, will resist thermal shock, possesses good adhesion to the glass in the presence of moisture

766196

and humidity, possesses a high tack point temperature, is adaptable to external coating by high speed dipping procedures, possesses good abrasion resistance and has good surface gloss.

As a possible alternative embodiment, the present coatings can be coated into a chimney shaped glass member which is adapted to be fitted over an incandescent lamp. Such a member, of course, is hollow and is adapted to surround a source of radiations such as an  
10 incandescent lamp or other type of light source.

While best embodiments of the invention have been illustrated and described in detail, it is to be particularly understood that the invention is not limited thereto or thereby.

766196

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1           1. A hollow light-transmitting glass member  
2 adapted to surround a source of radiations, a coating  
3 carried on the external surface of said glass member, said  
4 coating comprising a mixture of:

5           (a) a polymer consisting essentially of  
6 polymethylmethacrylate having a tack point temperature  
7 of at least 170°C. and an inherent viscosity of at least  
8 0.44;

9           (b) from 0.1% to 10% by weight of said poly-  
10 methylmethacrylate of an organofunctional silane having  
11 organic functional groups and silicon functional groups,  
12 organic functional group of said silane reacted with said  
13 polymethylacrylate and silicon functional groups of said  
14 silane reacted with the surface of said glass member to  
15 couple said polymethylmethacrylate to said glass member;  
16 and

17           (c) from 2% to 20% by weight of said poly-  
18 methylmethacrylate of an additive organic substance which  
19 is at least substantially transparent, has a boiling  
20 temperature at atmospheric pressure of at least 250°C.,  
21 and is completely soluble in said polymethylmethacrylate  
22 polymer within the temperature range of from -40°C to 170°C.

1           2. The coated glass member as specified in  
2 claim 1, wherein said glass member is a sealed envelope  
3 for an incandescent lamp, and said envelope encloses an  
4 incandescent filament.

766196

1 3. The coated glass member <sup>as</sup> ~~is~~ specified in  
2 claim 1, wherein said coating includes a coloring substance  
3 in predetermined quantity sufficient to impart a desired  
4 absorption of light to said coating.

1 4. The glass member as specified in claim 3,  
2 wherein said coloring substance comprises a dye dissolved  
3 in said coating.

1 5. The glass member as specified in claim 3,  
2 wherein said coloring substance comprises a pigment dis-  
3 persed throughout said coating.

1 6. The glass as specified in claim 1, wherein  
2 said coating has dispersed throughout a predetermined  
3 amount of very finely divided, light-scattering substance.

1 7. The coated glass member as specified in  
2 claim 1, wherein said silane is at least one material of the  
3 group consisting of N- $\beta$ -aminoethyl- $\delta$ -aminopropyl-  
4 trimethoxysilane,  $\delta$ -methacryloxypropyltrimethoxysilane,  
5  $\delta$ -glycidoxypropyltrimethoxysilane and vinyltriethoxy-  
6 silane.

1 8. The coated glass member as specified in  
2 claim 1, wherein said additive organic substance is at  
3 least one material of the group consisting of butyl benzyl  
4 phthalate, chlorinated biphenyl, butyl phthalyl butyl  
5 glycolate, N-ethyl toluene sulfonamide, tricresyl phosphate,  
6 and polyisobutylmethacrylate.

1 9. The coated glass member as specified in claim  
2 1, wherein said silane is at least one material of the group

3 consisting of N- $\beta$ -aminoethyl- $\gamma$ -aminopropyltrimethoxy-  
 4 silane,  $\gamma$ -methacryloxypropyltrimethoxysilane,  $\gamma$ -  
 5 glycidoxypropyltrimethoxysilane and vinyltriethoxysilane,  
 6 and wherein said additive organic substance is at least  
 7 one material of the group consisting of butyl benzyl ph-  
 8 thalate, chlorinated biphenyl, butyl phthalyl butyl gly-  
 9 colate, N-ethyl toluene sulfonamide, tricresyl phosphate,  
 10 and polyisobutylmethacrylate.

1 10. A hollow light-transmitting glass member  
 2 adapted to surround a source of radiations, a coating  
 3 carried on the external surface of said glass member, said  
 4 coating comprising a mixture of:

5 (a) a polymer consisting essentially of poly-  
 6 methacrylate having a tack point temperature of at  
 7 least 170°C., and an inherent viscosity of at least 0.44;

8 (b) from 0.3% to 3% by weight of said poly-  
 9 methacrylate of an organofunctional silane having  
 10 organic functional groups and silicon functional groups,  
 11 organic functional group of said silane reacted with said  
 12 polymethacrylate and silicon functional groups of said  
 13 silane reacted with the surface of said glass member to  
 14 couple said polymethacrylate to said glass member; and

15 (c) from 5% to 15% by weight of said methacrylate  
 16 of an additive organic substance which is at least sub-  
 17 stantially transparent, has a boiling temperature at at-  
 18 mospheric pressure of at least 250°C., and is completely  
 19 soluble in said methacrylate within the temperature range  
 20 of from -40°C. to 170°C.





766196

LAMP COATING

MODIFIED  
POLYMETHYLMETHACRYLATE  
COATING

